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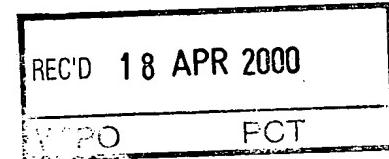
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**Patentanmeldung Nr. Patent application No. Demande de brevet n°**

99302127.8

## PRIORITY DOCUMENT

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**Blatt 2 der Bescheinigung  
Sheet 2 of the certificate  
Page 2 de l'attestation**

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**Primer coating of steel**

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**Primer Coating of Steel**

This invention relates to a process for the primer coating of steel. In particular, it  
5 relates to the coating of semi-finished steel products which are subsequently to  
be fabricated by heat-intensive processes and overcoated. Such semi-finished  
steel products are used in the shipbuilding industry and for other large-scale  
structures such as oil production platforms and include steel plates, for example  
10 of thickness 6 to 75 mm, bars, girders and various steel sections used as  
stiffening members. The most important heat-intensive process is welding;  
substantially all such semi-finished steel products are welded. Other important  
heat-intensive processes are cutting, for example oxy-fuel cutting, plasma  
15 cutting or laser cutting, and heat firing in which the steel is bent into shape while  
being heated. These steel products are often exposed to the weather during  
storage before construction and during construction, and they are generally  
coated with a coating called a "shop primer" or "pre-construction coating" to  
avoid corrosion of the steel occurring before the steel construction, e.g. ship, is  
given its full coating of anticorrosive paint, thereby avoiding the problem of  
having to coat over or remove steel corrosion products. In most big shipyards,  
20 the shop primer is applied as one of several treatments carried out on a  
production line in which the steel is for example preheated, shot- or grit-blasted  
to remove millscale and corrosion products, shop primed and passed through a  
drying booth. The shop primer can alternatively be applied by a trade coater or  
steel supplier before the steel is delivered to the shipyard or other construction  
25 site.

Although the main purpose of the shop primer is to provide temporary corrosion  
protection during construction, it is preferred by shipbuilders that the shop  
primer does not need to be removed but can remain on the steel during and  
30 after fabrication. Steel coated with shop primer thus needs to be weldable  
without removal of shop primer and to be overcoatable with the types of  
protective anti-corrosive coatings generally used on ships and other steel

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constructions, with good adhesion between the primer and the subsequently applied coating. The shop primed steel should preferably be weldable without significant detrimental effect on the quality of the weld or on the speed of the welding process and should be sufficiently resistant to heat that the shop primer 5 retains its anticorrosive properties in areas heated during fairing or during welding of the opposite face of the steel.

Commercially successful shop primers available today are solvent borne coatings based on prehydrolysed tetraethyl orthosilicate binders and zinc powder. Such coatings contain a large proportion of volatile organic solvent, typically about 650 grams per liter, to stabilize the paint binder and to enable the product to be applied as a thin film, typically about 20 microns thick. Release of volatile organic solvent can be damaging to the environment and is regulated by legislation in many countries. There is a need for a shop primer which releases 10 no, or much less, volatile organic solvent. Examples of such coatings are 15 described in US-A-4888056 and JP-A-7-70476.

JP-A-6-200188 is concerned with shop primer coatings and mentions the possibility of using an aqueous alkali silicate salt type binder. Coatings comprising an aqueous alkali metal silicate and zinc powder are also proposed 20 in GB-A-1226360, GB-A-1007481, GB-A-997094, US-A-4230496 and JP-A-55-106271. Alkali silicate binders for anticorrosive coatings are also mentioned in US-A-3522066, US-A-3620784, US-A-4162169 and US-A-4479824. We have found that primer coatings based on an aqueous alkali silicate binder containing 25 zinc powder can give adequate corrosion protection and allow the steel surfaces they cover to be welded but give rise to problems when overcoated. The aqueous silicates contain a large quantity of alkali metal cations which are required to keep the silicate in aqueous solution and these ions are still present in the coating after the coating has dried. We have found that, if primer coatings 30 having these large quantities of alkali metal ions are overcoated with any conventional organic coating and then immersed in water, blistering (local delamination of the topcoat) occurs.

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Aqueous silica sols having very low alkali metal ion content are available commercially but coatings based on such sols have very poor film strength in terms of adhesion, cohesion, hardness, and resistance to abrasion and water.

5 Suggested improvements to silica sol coatings are described in US-A-3320082, which adds a water-immiscible organic amine, GB-A-1541022, which adds a water-soluble acrylamide polymer and GB-A-1485169, which adds a quaternary ammonium or alkali metal silicate, but such coatings have not achieved physical properties similar to those of coatings based on alkali metal silicates. Coatings 10 based on silica sols show low levels of blistering when overcoated/immersed. Although the water soluble salt content and osmotic pressure is low, blistering still occurs as the coating exhibits little resistance to blister initiation/growth due to its poor physical properties.

15 There is a need for a water-based shop primer of low alkali metal ion content which has improved adhesion to substrates and film strength in terms of the properties discussed above to resist blister initiation and growth.

20 A process according to the present invention for primer coating of steel which is intended to be fabricated and overcoated, in which process the steel is primer coated with a primer coating comprising zinc powder and silica or silicate binder, is characterized in that the binder comprises an aqueous silica sol or alkali metal silicate having a  $\text{SiO}_2/\text{M}_2\text{O}$  mole ratio, where M represents total alkali metal and ammonium ions, of at least 6:1, and that after the primer 25 coating has dried to the extent that it is touch dry it is treated with a solution which increases the film strength of the primer coating.

The binder is most preferably an aqueous silica sol. Such sols are available from DuPont under the Registered Trademark "Ludox" or from Akzo Nobel 30 under the Registered Trademark "Bindzil", although the literature concerning them emphasizes that conventional grades of colloidal silica are not good film formers. Various grades of sol are available having various particle sizes and

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containing various stabilizers. The particle size of the colloidal silica can for example be in the range 3 to 100 nm; particle sizes towards the lower end of this range, for example 5 to 10 nm, are preferred. The silica sol preferably has a  $\text{SiO}_2/\text{M}_2\text{O}$  mole ratio of at least 25:1, more preferably at least 50:1 and may 5 have a  $\text{SiO}_2/\text{M}_2\text{O}$  mole ratio of 200:1 or more. The sol can be stabilized by alkali, for example sodium hydroxide or ammonium or quaternary ammonium hydroxide, or by a water-soluble organic amine such as alkanolamine.

The silica sol can be blended with an alkali metal silicate, for example lithium 10 silicate, sodium-lithium silicate or potassium silicate, or with ammonium silicate or a quaternary ammonium silicate. The addition of an alkali metal or ammonium silicate may improve the initial film-forming properties of the silica sol, but the amount of alkali metal silicate should be low enough to keep the  $\text{SiO}_2/\text{M}_2\text{O}$  mole ratio of the binder sol at least 6:1, preferably at least 8:1 and 15 most preferably above 15:1.

The silica sol can alternatively or additionally contain a dissolved or dispersed 20 organic resin. The organic resin is preferably a latex, for example a styrene butadiene copolymer latex or a styrene acrylic copolymer latex or a polyvinyl butyral dispersion. Water soluble polymers such as acrylamide polymers can be used but are less preferred. The organic resin is preferably used at up to 25% by weight, preferably 1-10% by weight, based on silica. Higher amounts may cause weld porosity during subsequent welding.

25 The silica sol can alternatively contain a silane coupling agent which contains alkoxy silane groups and an organic moiety containing a functional group such as amino, epoxide or isocyanate group. The silane coupling agent is preferably an aminosilane such as gamma-aminopropyl triethoxy silane or gamma-aminopropyl trimethoxy silane, or a partial hydrolysate thereof, although an epoxy silane such as gamma-glycidoxypipropyl trimethoxy silane can be used. 30 The silane coupling agent is preferably present at up to 30% by weight, for example 1-20% by weight, based on silica.

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The binder of the primer coating can alternatively comprise an aqueous solution of an alkali metal or ammonium silicate stabilized by a siliconate substituted by at least one anionic group of lower pKa than silicic acid such as a carboxylate or 5 sulphonate group, as described in British patent application 9823054.3. Such a binder is preferably a solution having a SiO<sub>2</sub>/M<sub>2</sub>O mole ratio in the range 8:1 to 30:1 and a pH of 7 to 10.5 prepared by lowering the pH of a solution of silicate and siliconate by cation exchange. For example the siliconate can be added at relatively low levels, for example at a molar ratio of 1:2 to 1:20, to a 10 conventional 3.9:1 SiO<sub>2</sub> : K<sub>2</sub>O alkali silicate. The solids may then be reduced to improve ease of processing and to further improve stability. At this stage the solution has a pH of 12-12.5. The solution is ion exchanged using a standard ion exchange resin. K<sup>+</sup> ions are replaced with H<sup>+</sup> reducing both the alkali content of the binder and the pH. Without the presence of the siliconate the silicate 15 would gel on reducing the pH. Clear, stable solutions with pH's as low as 8 have been obtained. The resultant binder has an SiO<sub>2</sub>:K<sub>2</sub>O mole ratio typically in the range 8-20:1 and can be concentrated if desired to increase the solids. The binder is a clear, stable solution and is stable in the presence of zinc but 20 coatings based on these ion exchanged binders have relatively poor film strength, compared to coatings based on alkali silicate binders.

The primer coating contains zinc powder, which is preferably of volume averaged mean particle size 2 to 12 microns and most preferably sold commercially as zinc dust having a mean particle size of 6 to 9 microns. The 25 zinc powder protects the steel by a galvanic mechanism and may also form a protective layer of zinc corrosion products which enhances the corrosion protection given by the coating. The amount of zinc powder in the coating is generally at least 10% and may be up to 90% by volume of the coating, on a dry film basis. The zinc powder can be substantially the whole of the pigmentation 30 of the coating or can for example comprise up to 70%, for example 25 to 55%, by volume of the coating, on a dry film basis with the coating also containing an auxiliary corrosion inhibitor, which can for example be a molybdate, phosphate,

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tungstate or vanadate, calcined clay or talc as described in US-A-5246488 and/or a filler such as silica, aluminum silicate, talc, barytes or mica. The pigment volume concentration of the primer coating is preferably at least equal to the critical pigment volume concentration, as is usual for zinc silicate primers,

5 for example 1.0 to 1.5 times the critical pigment volume concentration.

The solids content of the primer coating is generally at least 15% by volume and preferably in the range 20 to 35% by volume. The coating preferably has a viscosity such that it can easily be applied by conventional coating applicators 10 such as spray, particularly airless spray or high volume low pressure (HVLP) spray applicators, to give a coating of dry film thickness less than 40 microns, preferably between 12 and 25 to 30 microns.

The primer coating is dried to the extent that it is touch dry before it is treated 15 with the film strengthening solution. The time to touch dry is generally about 10 to 15 minutes at ambient temperatures of 15 to 20°C or 3 to 4 minutes at 40°C. Drying time is also dependent on air flow and film thickness. It may be preferred to carry out drying of the primer coating at 30-60°C, especially if primer coating, 20 drying and application of the film strengthening solution are to be carried out in an on-line process. Application of the treatment solution before the primer is dry does not give film strengthening.

The solution which increases the film strength of the primer coating can in general be an aqueous solution of an inorganic salt or a solution of material 25 having reactive silicon-containing groups. The increase in film strength can be detected by a significant increase in hardness, abrasion resistance and usually adhesion. Hardness can be measured in pencil hardness test British Standard 3900, part E19 (1999) (hardness of pencil required to gouge the coating). Abrasion resistance can be measured using a double rub test which 30 automatically rubs the coating and can be carried out dry or wet with water. While a significant increase in either dry or wet abrasion resistance would be regarded as an increase in film strength of the primer coating, we have found

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that the treatment according to the invention generally increases both dry and wet abrasion resistance. Adhesion can be measured by a cross-hatch test as described in British Standard 3900, part E6 (1992).

- 5 The amount of film strengthening solution applied to the primer coating is generally in the range 0.001-0.2 liters per square meter of primer coated surface ( $L/m^2$ ). Such an amount of solution can conveniently be applied by spraying. Washing has previously been suggested as a post-treatment for zinc silicate coatings based on an alkali metal silicate binder, but this has involved application of larger amounts of water to wash soluble alkali metal salts from 10 coatings having  $SiO_2:M_2O$  ratios of about 3:1 to 4:1. Application of water alone to the touch dry primer coatings of the present invention does not give substantial film strengthening.
- 15 While we do not wish to be bound by any theory explaining the film strengthening, it appears that when the treatment solution is an aqueous inorganic salt solution, either silica dissolution and reprecipitation takes place or the salt acts as a reinforcing agent between the sol particles. When the treatment solution contains reactive silica species, these can be deposited 20 between the silica sol particles to improve bonding of the sol particles. We have found that the same strengthening materials, when added to the primer coating composition at or before application to the substrate, do not strengthen the primer coating film formed.
- 25 When the film strengthening solution is an aqueous solution of an inorganic salt, it generally has a concentration of at least 0.01M and preferably at least 0.03M, most preferably at least 0.05M. The concentration of the inorganic salt solution can be up to 2M or 3M or even higher. The inorganic salt can be the salt of a monovalent cation such as an alkali metal or ammonium salt or of a divalent 30 cati n such as zinc, magnesium or calcium, and of a monovalent anion such as a halide, for xample fluoride, chlorid or bromide, or nitrate, or a polyvalent anion such as sulphate or phosphat . Mlxtures of th above-menti ned salts

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can also be used. Examples of inorganic salt solutions which have been found effective are magnesium sulphate, zinc sulphate, potassium sulphate, sodium chloride and potassium chloride, although chlorides may not be preferred because of their tendency to promote corrosion. The concentration of the

- 5      inorganic salt solution in weight terms is preferably in the range 0.5-20 % by weight.

One example of a material having active silicon-containing groups is a silicate.

The film strengthening solution can for example be an alkali metal silicate

- 10     solution, for example potassium silicate or lithium silicate, or an ammonium silicate solution or can be an alkali metal silicate, for example an alkylsiliconate solution. The preferred concentration of such a solution is in the range 0.5-20% by weight.

- 15     When the film strengthening solution is a solution of an inorganic salt or alkali metal silicate, the added material will increase the salt content of the zinc silicate primer coating. This will tend to increase the osmotic driving force when the coating is overcoated and thus the possibility of osmotic blistering when the coated substrate is immersed. The amount of inorganic salt of alkali metal silicate applied is preferably low enough so that the  $\text{SiO}_2/\text{M}_2\text{O}$  mole ratio of the primer coating binder is kept above 6:1, preferably above 8:1 and most preferably above 10:1. To achieve this, the amount of inorganic salt or alkali metal silicate applied in the film strengthening solution is preferably less than 10g/m<sup>2</sup> on a dry weight basis, most preferably less than 5g/m<sup>2</sup>.

- 25     An alternative example of a material having reactive silicon-containing groups is an alkoxy silane or an acyloxy silane, for example acetoxy silane. This can for example be a tetraalkoxy silane (alkyl orthosilicate) such as tetraethoxy silane or tetraisopropoxy silane, or a trialkoxy silane such as methyl trimethoxy silane. The alkoxy silane may contain additional functional groups, for example a trialkoxy silane can have the formula  $\text{RSI}(\text{OR}'_3)$  where each R' group is 1-3C alkyl and R is an alkyl or aryl group substituted by an amino, alkylamino,

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dialkylamino, amide, halogen, carbamate, epoxide, Isocyanate, aziridine, sulphonate, carboxylate, phosphate or hydroxyl group. Preferred examples are aminosilanes such as gamma-aminopropyl triethoxy silane ("Aminosilane A1110") or gamma-aminopropyl trimethoxy silane. The alkoxy silane can be a

5 bis(trialkoxy silane), for example an alkylene or polydimethylsilane chain tipped with -SiOR<sub>3</sub> groups. The alkoxy silane can be at least partially hydrolyzed, for example a partially hydrolyzed tetraalkoxy silane such as the material sold commercially as "Ethyl silicate 40", or a hydrolyzed alkyl trialkoxy silane or aminoalkyl trialkoxy silane, can be used. The alkoxy silane is preferably applied from aqueous solution, although the aqueous solution can contain a water-miscible organic solvent, for example an alcohol such as ethanol. The concentration of alkoxy silane in the treatment solution is preferably in the range 1-25% by weight.

10 The application of the treatment solution, and preferably also the drying of the treated primer coating until the coating is again touch dry, can be carried out in an on-line process following primer coating of the steel and drying of the primer coating until it is touch dry. The amount of film strengthening solution applied is preferably 0.005-0.1 L/m<sup>2</sup> of primer coated surface, most preferably 0.05 L/m<sup>2</sup> or less if the coating is treated and dried on-line. The drying time for a coating treated with this amount of film strengthening solution is generally about 5 to 10 minutes at 15-20°C or about 1.5 to 2 minutes at 40°C. The treatment solution is 15 preferably applied and dried at a temperature in the range 30-60°C. The treatment solution can be applied by standard spray application equipment, for 20 example airless spray or HVLP spray, or by a simple atomizer spray, simply by mounting a second spray gun further down the shop primer line from the spray gun applying the primer. The treatment solution can be applied to both sides of 25 a substrate, for example to both sides of a steel plate for use in shipbuilding, whatever the orientation of the substrate; the volume of solution required to strengthen the film are such that the solution can be applied to the und side of 30 a plat without sagging or dripping. Other methods of application such as application by roller are possible but are not preferred. The treated primer

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coating only needs to be allowed to dry on the substrate and does not need any subsequent washing or heating; once the treated primer is dry the coated product can be handled normally.

- 5 The treatment process according to the Invention increases the hardness, cohesion and abrasion resistance of the shop primer without introducing the disadvantage of blistering when overcoated. For example when a zinc-filled silica sol coating is treated, the dry abrasion resistance is increased at least fivefold and the wet abrasion resistance usually tenfold or more. The pencil
- 10 hardness typically changes from 2B to H or harder. The SiO<sub>2</sub>/M<sub>2</sub>O mole ratio of the primer coating may for example be reduced from 50-200 to 15-35 if the film strengthening solution applied is an inorganic salt solution or alkali metal silicate solution, but at normal dry film thickness of 15-20 µm for shop primer coatings this is still above the level at which significant blistering occurs. The SiO<sub>2</sub>/M<sub>2</sub>O
- 15 mole ratio can be maintained at an even higher level if the film strengthening solution is an alkoxy silane solution. The treated primer coatings can be overcoated with an amine-cured epoxy resin coating, or any other heavy duty coating such as a polyurethane, at a film thickness of 100 µm or 200 µm and after being allowed to cure for 7 days can be immersed in fresh or sea water for
- 20 over 2 weeks at 40°C, or 3 months at 15°C, without blistering.

The Invention is illustrated by the following Examples:-

**Examples 1 to 7**

25

A primer coating of solids concentration 25% by volume was prepared from the following ingredients. The primer coating had a pigment volume concentration of 74.6%, which is 1.3 times the critical pigment volume concentration ( $\lambda = 1.3$ ).

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## % by weight

Ludox® SM (a silica sol of concentration 30% by weight, particle size 7 nm and SiO <sub>2</sub> /M <sub>2</sub> O ratio 50:1)	25.8
water	20.4
Bentonite clay thixotropic	0.2
Zinc dust	45.5
Satintone® aluminosilicate extender pigment	8.1

5 A primer was prepared by mixing the silica sol with water and thixotropic and the resulting binder was mixed with the pigments just before application to the steel, as is usual with zinc silicate coatings. The obtained primer coating was applied to 15 cm x 10 cm steel panels at a dry film thickness of 15-20 µm. The primer was allowed to dry overnight at ambient temperature.

10 The panels were then sprayed with various film strengthening solutions. The inorganic salts had a concentration of 5% by weight and the silicon-containing solutions had a concentration of 8% by weight and 0.2 cm<sup>2</sup> of the solution was sprayed on each panel. The treated coating was allowed to dry at 15-20°C for at least 1 hour and was then tested for pencil hardness (BS 3900:E19), cross-hatch adhesion (BS 3900:E6) on a scale rated from 0 (no adhesion) to 5 (100% adhesion) and abrasion resistance (double rub test). In the double rub test the treated surface is wetted with a couple of drops of water (if doing wet double rubs) then rubbed with a cotton wool swab using light pressure. One pass to and from is a double rub. The results are expressed as the number of double rubs till removal of the coating. If the coating survives 100 double rubs the final dry film thickness (dft) is compared to the initial value. If the dft is reduced by more than 25% the result is expressed as >100. If the dft is reduced by less than 25% the result is expressed as >>100. The same tests were carried out in comparative experiments on (C1) an untreated primer coating and (C2) a primer

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coating which had been sprayed with 0.2 cm<sup>3</sup> water. The results are shown in Table 1 below.

Table 1

Example No	Additive and concentration	Mechanical properties of treated coatings		
		Double rubs Dry/Wet	Pencil Hardness	Cross-hatch Adhesion
C1	Control	22/8	2B	0
C2	Water (sprayed)	35/12	B	1
1	5% Potassium chloride	>>100/>>100	6-9H	2-3
2	5% Potassium sulphate	>>100/50	H-2H	3
3	5% Zinc sulphate	>>100/50-100	H	3
4	8% Potassium silicate	>>100/>>100	5H	3-4
5	8% TEOS/water (pH=2)	>>100/50	5H	1
6	8% TEOS/alcohol	>>100/100	HB	1
7	5% Aminosilane A1110/water	>>100/>>100	6H	2-3

5

The potassium silicate solution of Example 4 had a SiO<sub>2</sub>/M<sub>2</sub>O ratio of 3.9:1.

Example 5 used tetraethyl orthosilicate (TEOS) partially hydrolyzed in water at pH=2.

Example 6 used TEOS hydrolyzed in water and diluted with an equal volume of ethanol.

### Examples 8 and 9

Primer coatings were prepared using the formulation of Example 1 but with the following silica sols used in place of Ludox SM:-

Example 8 - Ludox AM, a sol of particle size 12 nm and SiO<sub>2</sub>/M<sub>2</sub>O ratio 125:1.

Example 9 - Bindzill 5080, a polydisperse sol of average particle size 40 nm and SiO<sub>2</sub>/M<sub>2</sub>O ratio 225:1.

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Example 10

A primer coating was prepared based on Ludox SM silica sol and zinc but  
 5 having the formulation shown below. The coating had a pigment volume  
 concentration of 81% ( $\lambda=1.3$ )

Component	% by weight
Ludox SM sol (30 wt.% solids)	19.0
Water	24.7
Bentonite clay thixotrope	0.2
Zinc dust	45.0
Satintone pigment	3.4
"Molywhite" molybdate pigment	7.7

10

Example 11

A primer coating was prepared using the ingredients of Example 1 but with the amount of each pigment component proportionally reduced so that the pigment volume concentration was equal to the critical pigment volume concentration.

15

The coatings of Examples 8 to 11 were applied to steel panels and allowed to dry as described in Example 4. The panels were then sprayed with 0.2 cm<sup>3</sup> of a 8% by weight potassium silicate solution as used in Example 4. The panels were tested as described in Example 1, except that no comparison was done 20 with a primed panel sprayed with water. The results are shown in Tables 2a and 2b below.

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**Table 2a**

Example No.	Sol/Formulation	Mechanical properties of untreated coatings		
		Double rub Dry/Wet	Pencil Hardness	Cross-hatch Adhesion
8	Ludox AM/ $\lambda$ =1.3	30/10	2B	2
9	Bindzil 5080/ $\lambda$ =1.3	4/1	H	3
10	Ludox SM/ $\lambda$ =1.3	10/4	4B	1
11	Ludox SM/ $\lambda$ =1.0	20/5	B	0

5

**Table 2b**

Example No.	Sol/Formulation	Mechanical properties of treated coatings		
		Double rub Dry/Wet	Pencil Hardness	Cross-hatch Adhesion
8	Ludox AM/ $\lambda$ =1.3	100/75-100	H-3H	2
9	Bindzil 5080/ $\lambda$ =1.3	100/40-100	4H	3-4
10	Ludox SM/ $\lambda$ =1.3	>>100/80-100	5H	3
11	Ludox SM/ $\lambda$ =1.0	>>100/80	HB	0

Examples 4, 8 and 9 show that film strengthening is achieved for a variety of sols and coating compositions, with better treated coatings obtained from sols of smaller particle size.

10

Examples 4 and 11 show that best results are achieved at a higher than critical pigment volume concentration.

**Examples 12 to 15**

15

The process of Example 4 was repeated using different concentrations of potassium silicate solution. The panels were tested after drying and the results are shown in Table 3 below. These results show that a strengthening effect is

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achieved even using potassium silicate at a concentration of 0.5% by weight, the effect increasing with concentration up to 4%.

**Table 3**

5

Example No	Potassium silicate concentration	Mechanical properties of treated coatings		
		Double rub Dry/Wet	Pencil Hardness	Cross-hatch Adhesion
4	8 wt.%	>>100/>>100	5H	3-4
12	4 wt.%	>>100/>>100	5H	3-4
13	2 wt.%	>>100/60	6H	3-4
14	1 wt.%	>>100/40	2H	4
15	0.5 wt.%	100/20	HB	4

**Example 16**

10

To simulate practical application of the film strengthening solution, Example 4 was repeated with application of the potassium silicate after only 10 minutes or 30 minutes drying of the primer coating at 20°C.

- 15 The drying time of 10 minutes at 20°C was sufficient for some panels to become touch dry but others were still partly wet (that is, they had no surface water but were wet to the touch over at least part of the panel). All panels dried for 30 minutes at 20°C were touch dry. On testing as described in Example 1, markedly different results were obtained depending on whether the primer 20 coated panel was touch dry when the potassium silicate was applied, as shown in Table 4 below.

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Example 17

Example 16 was repeated but with drying of the primer coating at 40°C. The primer was observed to become touch dry in 3 or 4 minutes. Panels dried at 5 40°C for 4 minutes were tested as described in Example 1 and the results are included in Table 4 below.

Table 4

Example No	Drying time and temperature	Appearance on applying additive	Double Rub Dry/Wet	Pencil Hardness	Cross-hatch Adhesion
16	10 min at 20°	Partly wet	13/4	2B	0
	10 min at 20°C	Dry	>>100/>>100	6H	3-4
	30 min at 20°C	Totally dry	>>100/>>100	6H	3-4
17	4 min at 40°C	Totally dry	>>100/>>100	3H	4

10

Examples 18 and 19

A hybrid silica sol organic resin primer coating was prepared from the following 15 ingredients and applied to steel panels as described in Example 1.

Component	Amount (% by weight)
Ludox SM sol (30 wt % solids)	19.8
Dow 94770 Styrene butadiene latex (50% solids)	3.6
Water	23.0
Bentonite clay thixotrope	0.2
Satin tone	8.1
Zinc	45.5

Panels were sprayed with 0.2 cm<sup>2</sup> of an 8% by weight potassium silicate solution (Example 18) or of a 5% by weight aqueous amin silane solution

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(Example 19) and allowed to dry and tested as described in Example 1. The results obtained are shown in Table 5 below:

**Table 5**

5

Example No.	Treatment	Mechanical properties		
		Double rubs Dry/Wet	Pencil Hardness	Cross-hatch Adhesion
(Comparison)	Untreated	>>100/20-80	B	4
18	8% potassium silicate	>>100/>>100	6H	4
19	5% amino silane (A1110)	>>1000/>100	2H	5

**Examples 20 and 23**

10 The coatings of Examples 8 to 11 were applied to steel panels and allowed to dry as described in Example 4. The panels were then sprayed with 0.2 cm<sup>3</sup> of a 5% by weight potassium chloride solution. The panels were tested as described in Example 1, except that no comparison was done with a primed panel sprayed with water. The results are shown in Tables 6.

15

**Table 6**

Example No.	Treatment	Mechanical properties		
		Double rubs Dry/Wet	Cross-hatch Adhesion	Pencil Hardness
20	8 + 8% potassium chloride	100/50	3	5H
21	9 + 8% potassium chloride	100/10	3	3H
22	10 + 8% potassium chloride	>>100/20-30	2	2H
21	11 + 8% potassium chloride	>>100/50	0-1	HB

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Claims

1. A process for primer coating of steel which is intended to be fabricated and  
5 overcoated, in which process the steel is primer coated with a primer  
coating comprising zinc powder and a silica or silicate binder, characterized  
in that the binder comprises an aqueous silica sol or alkali metal silicate  
having a  $\text{SiO}_2/\text{M}_2\text{O}$  mole ratio, where M represents total alkali metal and  
ammonium ions, of at least 6:1, and that after the primer coating has dried  
10 to the extent that it is touch dry it is treated with a solution which increases  
the film strength of the primer coating.
2. A process according to claim 1, characterized in that the touch dry primer  
coating is sprayed with the film strengthening solution.  
15
3. A process according to claim 1 or claim 2, characterized in that the binder is  
a silica sol of  $\text{SiO}_2/\text{M}_2\text{O}$  mole ratio at least 25:1.
4. A process according to claim 1 or claim 2, characterized in that the binder  
20 comprises an aqueous solution of an alkali metal or ammonium silicate  
stabilized by a siliconate substituted by at least one anionic group of lower  
pKa than silicic acid, having a pH of 7 to 10.5 prepared by lowering the pH  
of a solution of silicate and siliconate by ion exchange.
- 25 5. A process according to any of claims 1 to 4, characterized in that the touch  
dry primer coating is treated with an aqueous solution of an inorganic salt of  
concentration at least 0.01M.
- 30 6. A process according to any of claims 1 to 5, characterized in that the touch  
dry primer coating is treated with a solution of a silicate or alkoxysilan .

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7. A process according to any of claims 1 to 6, characterized in that the solution is applied to the touch dry primer coated steel at 0.001-0.2 liters per square meter primer coated surface.
- 5 8. A process according to any of claims 1 to 7, characterized in that the primer coating of the steel, drying of the primer coating until it is touch dry and application of the treatment solution are carried out successively in an on-line process.
- 10 9. Use of an aqueous solution of an inorganic salt of concentration at least 0.01M as a spray treatment of steel primer coated with a primer coating comprising zinc powder and an aqueous silica sol or alkali metal silicate binder having a  $\text{SiO}_2/\text{M}_2\text{O}$  mole ratio, where M represents total alkali metal and ammonium ions, of at least 6:1.
- 15 10. Use of a silicate or alkoxy silane solution as a spray treatment of steel primer coated with a primer coating comprising zinc powder and an aqueous silica sol or alkali metal silicate binder having a  $\text{SiO}_2/\text{M}_2\text{O}$  mole ratio, where M represents total alkali metal and ammonium ions, of at least 6:1.
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